Resumen
En el presente trabajo se estudió el comportamiento frente a la corrosión de cuatro aceros inoxidables, en biodiesel de soja a temperatura ambiente. Los aceros inoxidables utilizados fueron: AISI 304L, AISI 316, Sea Cure-1 y 2205. Se midieron las velocidades de corrosión aplicando métodos electroquímicos y mediante ensayos de pérdida de peso. Los estudios electroquímicos realizados fueron curvas de polarización potenciodinámica, medidas del potencial de circuito abierto en función del tiempo, y medidas de Espectroscopía de Impedancia Electroquímica. Además, se realizaron ensayos gravimétricos siguiendo la Norma ASTM G 31-72. Se obtuvieron bajas velocidades de corrosión para los cuatro aceros inoxidables, siendo siempre menor la velocidad de corrosión del acero 2205. Esto indica que los materiales estudiados son adecuados para utilizarse en contacto con biodiesel obtenido a partir de aceite de soja. La concordancia obtenida en los resultados al aplicar los diferentes métodos, permite concluir que los técnicas electroquímicas son adecuados para evaluar velocidades de corrosión de en biodiesel.

Palabras clave: Biodiesel; Corrosión; Aceros Inoxidables; Polarización Lineal; Ensayos Gravimétricos; Espectroscopía de Impedancia Electroquímica (EIE).

Abstract
In the present research we studied the behavior against corrosion of four stainless steels in soy biodiesel at room temperature. The stainless steels used were AISI 304L, AISI 316, Sea Cure-1 and 2205. The corrosion velocities were measured by applying electrochemical tests and weight loss methods. The electrochemical studies conducted were potentiodynamic polarization curves, measurement of the open circuit potential as a function of time, and Electrochemical Impedance Spectroscopy (EIS) measurements. In addition, gravimetric tests were performed according to ASTM G 31-72. The four stainless steels showed low corrosion rates being steel 2205 the one which always showed the lowest value. This indicates that the materials studied are suitable for use in contact with biodiesel obtained from soy oil. The agreement obtained in the results by applying different methods allows us to conclude that the electrochemical techniques are suitable to evaluate corrosion rates in soy biodiesel.

Keywords: Biodiesel; Corrosion; Stainless steels; Linear polarization; Gravimetric tests; Electrochemical Impedance Spectroscopy (EIS).

Introduction
The gradual replacement of fossil fuels by other forms of energy is a topical subject. This is due to the depletion of petrochemical reserves as well as to the awareness to preserve the environment. In this regard, biodiesel is of great interest as an ecologically sound source of energy.
techniques require short measurement times, have virtually unlimited sensitivity, and allow continuous monitoring of corrosion. The disadvantage is that they need to disturb the system by imposing an external polarization, which can cause changes in the specific properties of the system [25].

### Experimental

The stainless steels used were the austenitic steels AISI 304L and AISI 316, the ferritic steel Sea Cure-1 and the duplex steel 2205. Table 1 shows the compositions of these materials. Working electrodes of different steels studied were obtained (area exposed: 10 mm x 10 mm), and, before each test, the electrodes were polished with SiC paper of different granulometry up to # 1500, rinsed with deionized water, and dried by natural airflow.

An electrochemical cell of Pyrex® glass with three electrodes (ASTM G-5), with a reference electrode of Ag/AgCl and platinum counter, was used for the electrochemical tests. The solution used for the electrochemical measurements was an industrial biodiesel produced from soy oil. The properties of this biodiesel were determined according to ASTM and EN standards and are shown in Table 2.

#### Table 1: Chemical composition of the four stainless steels studied.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Method</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAME Contents, wt%</td>
<td>EN 14103:2011</td>
<td>99.10</td>
</tr>
<tr>
<td>Density 15ºC, kg/m³</td>
<td>ASTM D-1298-12b</td>
<td>885.90</td>
</tr>
<tr>
<td>Kinematic Viscosity 40 ºC, mm²/s</td>
<td>ASTM D-445-12</td>
<td>4.01</td>
</tr>
<tr>
<td>Corrected Flash Point ºC</td>
<td>ASTM D93-13el</td>
<td>167.00</td>
</tr>
<tr>
<td>Total contamination, mg/kg</td>
<td>EN 12662:1998</td>
<td>10.50</td>
</tr>
<tr>
<td>ColdS/eakFilterability, s</td>
<td>ASTM D-6751-09</td>
<td>302.00</td>
</tr>
<tr>
<td>Water Content, wt%</td>
<td>ASTM D-4928-12</td>
<td>0.04</td>
</tr>
<tr>
<td>Monoglyceride Content, wt%</td>
<td>UNE EN 14105:2003</td>
<td>0.65</td>
</tr>
<tr>
<td>Diglyceride Content, wt%</td>
<td>UNE EN 14105:2003</td>
<td>0.19</td>
</tr>
<tr>
<td>Triglyceride Content, wt%</td>
<td>UNE EN 14105:2003</td>
<td>0.03</td>
</tr>
<tr>
<td>Free Glycerol, wt%</td>
<td>UNE EN 14105:2003</td>
<td>0.01</td>
</tr>
<tr>
<td>Total Glycerol, wt%</td>
<td>UNE EN 14105:2003</td>
<td>0.21</td>
</tr>
<tr>
<td>Acid Number, mgKOH/g</td>
<td>ASTM D-644-11a</td>
<td>0.27</td>
</tr>
<tr>
<td>Oxidation/Stability, hours</td>
<td>EN 14112:2003</td>
<td>9.90</td>
</tr>
<tr>
<td>Cloud Point, ºC</td>
<td>ASTM D-2500-11</td>
<td>1.00</td>
</tr>
</tbody>
</table>

#### Table 2: Properties of the soy biodiesel used for the electrochemical measurements.

- Table 1: Chemical composition of the four stainless steels studied.
- Table 2: Properties of the soy biodiesel used for the electrochemical measurements.
Due to the high resistivity of the biodiesel, an aqueous extraction was performed to obtain the aqueous ionic fraction of the biofuel, which generates the corrosion process. A quantity of 150 ml of biodiesel and 300 ml of deionized water were measured, mixed for 10 minutes to form an emulsion, and allowed to stand for 20 hours in a separating funnel. After elapsed, the aqueous phase was used as a medium for electrochemical assays [22]. The tests were conducted in a naturally aerated environment and at room temperature (25-30°C).

The corrosion rates were measured by three different methods and the results were compared. On the one hand, electrochemical techniques based on the Stern-Geary equation were used, calculating the polarization resistance, $R_p$ for the method of Linear Polarization and Electrochemical Impedance Spectroscopy (EIS), and on the other hand, a Gravimetric Test was carried out. The Stern-Geary equation [25] relates the density of corrosion current, $i_{corr}$, with $R_p$, for simple reactions, controlled by the charge transfer (Eq. 1).

$$i_{corr} = \frac{babc}{2.303 (ba + bc)} \frac{1}{R_p} = \frac{B}{R_p}$$

Where $ba$ and $bc$ are the anodic and cathodic Tafel slopes, respectively. To determine the Tafel slopes, potentiodynamic polarization curves were obtained in a reduced potential range of ± 30 mV of the corrosion potential $E_{corr}$. According to the Linear Polarization Method [25], $R_p$ can be obtained graphically as the tangent to the curve $E_{corr}$ (Eq. 2).

$$R_p = \left( \frac{dE}{di} \right)_{E_{corr}}$$

Measurements of EIS were also made with different previous immersion times (0, 1, 3 and 5 hours), using Gamry® Reference 300 potentiostat/galvanostat with an initial period of system stabilization of 600 seconds to determine the open circuit potential, $E_{oc}$, and a potential amplitude of 10 mV around this potential. To adjust the results, the method of nonlinear least squares designed by Bouckamp was used. According to the EIS technique [25], $R_p$ values were obtained from the Nyquist plots, considering the following definition (Eq. 3).

$$R_p = \lim_{n \to 0} Z'$$

where $Z'$ represents the real part of the complete faradaic impedance. Applying Faraday’s law (Eq. 4) [26], the corrosion current density, $i_{corr}$, became the rate of penetration of the material, $V_{corr}$ expressed in mpy.

$$V_{corr} = \frac{PM}{nF \rho} i_{corr}$$

Where $PM$ is the molecular mass of the material, $n$ is the number of electrons exchanged, $\rho$ is the material density and $F$ is the Faraday constant.

Gravimetric tests were performed following the ASTM G31-72 standard norm. The test samples of AISI 304L (width: 2.61, length: 5.04 cm and thickness 0.30 cm), AISI 316 (width: 2.54 cm, length: 4.94 cm and thickness: 0.30 cm), Sea Cure-1 (width: 2.50 cm, length: 4.98 cm and thickness: 0.06 cm) and 2205 (width: 2.48 cm, length: 5.00 cm and thickness: 0.14 cm) were grounded with SiC paper up to #1500, and then were degreased with demineralized water and detergent, rinsed with alcohol and dried with airflow. The dried specimens were weighed on analytical balance with an accuracy of 0.0001 g. For immersion, the samples were clamped with plastic tweezers and placed inside glass containers containing pure biodiesel, ensuring that the coupons remained completely submerged in the medium. Special care was taken to ensure that the metal springs of the tweezers had no contact with the samples or biodiesel.

Figure 1 shows the coupons immersed in biodiesel. After 383 days (9192 hours) of exposure, the samples were extracted and their appearance regarding deposits, corrosion products or pit presence was examined. Demineralized water and detergent were used to remove fatty material, and then the coupons were placed in beakers containing alcohol to carry out ultrasound for 5 minutes to eliminate products that could be attached to the surface affecting the final weight measurement. The coupons were then dried with airflow and weighed again on the analytical balance to determine the weight change. The corrosion rate was calculated from (Eq. 5) [11,17]:

$$V_{corr (mpy)} = \frac{K \times W}{A \times T \times \rho}$$

where $K$ is a constant to unify units, which equals to 87 600 (h · cm) / (cm · year), $W$ is the area of the coupons in cm$^2$, $T$ is the exposure time in hours and $\rho$ is the density of material in g/cm$^3$. 

**Figure 1:** Steel coupons arranged for the immersion test in soy biodiesel.
Results and Discussion

The potentiodynamic curves obtained for the four steels studied in biodiesel were very similar (Figure 2). The materials maintained their passivity to very high values of potential. Steel 2205 presented the noblest Ecorr value, equal to -37 mV. This result is consistent with the expected behavior against corrosion for steel compared to other duplex steels. Because duplex stainless steels have a lower density of nonmetallic inclusions and secondary phases than single-phase stainless steels, it can be expected that they have higher resistance to corrosion than austenitic or ferritic steels [27-29].

Figure 2: Potentiodynamic curves of the four steels studied in the biodiesel extract.

Figure 3 shows the evolution of Eoc versus time for the materials studied. It is observed that the four alloys are stabilized, although they require different times for this. Steels AISI 316 and 2205 are the first to achieve stable potentials during the first 2 hours. Austenitic steel 304L requires approximately 3 hours to stabilize. Although steel Cure-1, among the four materials, shows the least favorable response, the stability of the potential reached after 5 hours indicates a good behavior against corrosion in this medium. According to Hodges, a ferritic alloy of high purity has outstanding resistance to attack in a wide variety of media containing chloride ion and organic acids [30].

Table 3 shows the Ecorr for the steels studied in the biodiesel extract, as well as the values of Eoc at which the samples were stabilized after 8 hours of exposure after 8 hours.

Once the balance was achieved, these potentials remained constant over time, and there was no sign of localized attack, so it can be deduced that the four stainless steels studied are resistant to pitting in the biodiesel extract studied [27].

Table 3: Ecorr and Eoc potentials.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Ecorr (mV)</th>
<th>Eoc after 8h (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304L</td>
<td>-227.00</td>
<td>46.00</td>
</tr>
<tr>
<td>AISI 316</td>
<td>-55.00</td>
<td>19.60</td>
</tr>
<tr>
<td>Sea cure-1</td>
<td>-152.00</td>
<td>-0.28</td>
</tr>
<tr>
<td>2205</td>
<td>-37.00</td>
<td>41.00</td>
</tr>
</tbody>
</table>

Figure 4: shows the Nyquist plots for different immersion times until 5 hours, and the enlargement of the capacitive arcs with increasing immersion time. The equivalent circuit used to adjust the impedance results obtained for the four materials at different immersion times is shown in the insert of Figure 4. This circuit is usually used to describe the behavior of stainless steels in different media, indicating the physical meaning of the elements [15,31-33]. RΩ corresponds to the resistance of the electrolyte, Rp is the polarization resistance due to the charge transfer resistance and CPEdl represents a constant phase element associated with the charge transfer.
The increase in polarization resistances $R_p$, which would result in a decrease in corrosion currents [24], is shown in Figure 5. This would indicate an increase in corrosion resistance over time [20], matching with that observed in Figure 3 about the evolution of the open circuit with time.

The values of $i_{corr}$ and $R_p$ coincide with those presented by Deyab & Keera [34], when evaluating the corrosion behavior of carbon steel in biodiesel, obtained from used cooking oil, using electrochemical techniques.

Table 5 shows the values of corrosion rate measured for the four materials by the three techniques used. VCorrP is the corrosion rate calculated from $R_{pPol}$, VCorrEIS was calculated from $R_{pEIS}$ and VCorrG is the corrosion rate measured by gravimetric test. The duplex stainless steel 2205 showed the lowest corrosion rate, whereas the ferritic stainless steel Sea cure-1 showed the highest corrosion rate. Austenitic stainless steels showed intermediate values of Vcorr. The fact that the sequence of velocity values from lower to higher was fulfilled for the four materials in the three methods indicates good agreement between the methods.

The velocities measured by the gravimetric method were markedly lower than those obtained by electroche-
The four materials showed very low corrosion rates, in the order of 1 micron/year by electrochemical methods, and even lower by gravimetric tests.

For stainless steel Q235 evaluated in rapeseed biodiesel at 43 °C for 60 days, E. Hu et al. found a corrosion rate of 1.50E-03 mpy, a value similar to the instantaneous velocities. In contrast, working with stainless steels 304, 444 and 439 for a time period similar to that tested in the gravimetric tests in this study (300 days), E. Miranda [19] found velocities in the order of 10-6 mpy, similar to the time-averaged velocities, VCorrG. For steel AISI 316 in palm biodiesel and working at 80 °C, M. Fazal et al. [11] found a corrosion rate of 1.15E-2 mpy. According to these authors [36], it is expected that this velocity value is greater than those presented in Table 6, because the values were obtained working at a higher temperature.

There is evidence of diversity in the results of corrosion rates of ferrous materials in different types of biodiesel. In the literature it is reported that the compatibility of a material and the biodiesel with which it is in contact, will depend on the origin of the biofuel [4,9,18,37]. This may be explained by the fact that some authors consider the presence of short chain organic acids as responsible for increasing the corrosivity of biodiesel.

The appearance of these acids is due to the oxidation of the unsaturated fatty acids contained in biodiesel [1,3,14]. The amount and type of saturated and unsaturated fatty acids that biodiesel will contain will depend on the raw material used for its production [8].

In future works the evaluation of the corrosion rates of these materials in biodiesel, with different contents of unsaturated fatty acids, will be carried out to obtain more precise information in this respect.

### Table 5: Corrosion rates obtained by the three methods (Linear Polarization and Electrochemical Impedance Spectroscopy and Gravimetric).

<table>
<thead>
<tr>
<th>Material</th>
<th>Vcorr</th>
<th>Vgrav</th>
<th>VcorrP</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304L</td>
<td>3.22E-03</td>
<td>2.90E-03</td>
<td>1.54E-05</td>
</tr>
<tr>
<td>AISI 316</td>
<td>2.26E-03</td>
<td>1.33E-03</td>
<td>1.21E-05</td>
</tr>
<tr>
<td>Sea cure-1</td>
<td>5.13E-03</td>
<td>5.73E-03</td>
<td>1.91E-05</td>
</tr>
<tr>
<td>2205</td>
<td>2.17E-03</td>
<td>1.20E-03</td>
<td>9.20E-06</td>
</tr>
</tbody>
</table>

The four stainless steels studied have good corrosion resistance and can therefore be used in contact with soy biodiesel. The materials behaved similarly in the medium studied, with low rates of corrosion, with duplex steel 2205 showing the lowest corrosion rate with the three methods used.

The comparison of the three methods to measure corrosion rates indicates good agreement between the results of electrochemical methods. Compared with the values obtained with the gravimetric method; the instantaneous velocities were higher and can be used as a safe value for this design. The application of electrochemical techniques to determine the corrosion rates in the biodiesel extract was satisfactory, because they have the advantage of reduced test time. These results can be supplemented by other electrochemical tests, such as measurement of open circuit potential over time or EIS measurements with different immersion times, to obtain an approximation of the kinetic behavior of the electrochemical process.

### List of Symbols

- $R_p$: Polarization resistance due to the charge transfer resistance
- $i_{corr}$: Corrosion current density
- $b_a$: Anodic Tafel slope
- $b_c$: Cathodic Tafel slope
- $E_{corr}$: Corrosion potential
- $PM$: Molecular mass of the material
- $\rho$: Material density
- $n$: Number of electrons exchanged
- $F$: Faraday constant
- $V_{corr}$: Corrosion rate
- $K$: Constant to unify units, which equals to $8.7 \times 10^{-9} (\text{h} \cdot \text{cm}) / (\text{cm} \cdot \text{year})$
- $W$: Area of the coupons in cm$^2$
- $T$: Exposure time in hours
- $E_{ocp}$: Open circuit potential
- $R_e$: Resistance of the electrolyte
- $CPE_{dl}$: Represents a constant phase element associated with the charge transfer
- $R_{pEIS}$: Polarization resistance calculated from the tangent of the polarization curve at the corrosion potential
- $R_{pPol}$: Polarization resistance calculated from plots of impedance spectra
- $V_{corr}$: Corrosion rate calculated from $R_{pEIS}$
- $V_{corrP}$: Corrosion rate measured by gravimetric test calculated from $R_{pEIS}$
- $V_{corrG}$: Corrosion rate measured by gravimetric test.

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